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BUREAU OF MINES
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INFORMATION CIRCULAR

FLUORESCENT MINERALS USED IN LIGHTING AND ELSEWHERE

BY

OLIVER C. RALSTON AND A. GEORGE STERN

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FLUORESCENT MINERALS USED IN LIGHTING AND ELSEWHERE 1/

By Oliver C. Ralston 2/ and A. George Stern 3/

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PURPOSE OF THIS REPORT

Fluorescence is of growing interest to the mineral industry becaus certain minerals may be detected thereby and because, as shown in figur 1,4/ many minerals (natural or synthetic) are needed in tubes and lamps. The use of fluorescent lighting is expanding, and large numbers of lamps of many sizes and shapes are being made and used in works, factories, stores, offices, homes, and in photography. Fluorescent tubes, as distinguished from clear tubes filled with neon, argon, or other rare gases through which a current of electricity passes, fluoresce owing to special selected and prepared minerals placed in the tubes. Luminous chemical and paints also contain special minerals and are used in similar applicat therefore, these also will be considered in this report.

Although the quantity of minerals (in tons) that are used for fluorescent purposes is small, and probably will continue to be so, this use i significant because it exemplifies a requirement for "pure" minerals in which a trace of contaminant as minute as one part in ten million may di tinguish between the acceptance or rejection of a particular material. T extreme purity makes synthetic minerals almost essential, and natural minerals are now little used.

Interest in fluorescent lighting has become so lively recently that this brief report has been prepared to answer a few of the numerous questions that arise in connection with minerals related to fluorescence.

FLUORESCENCE - WHAT IT IS

The fundamental principles of fluorescence are discussed by Fond At a low order of brightness, it is found in many organic products of our daily life and in minerals. Fluorescent solids among artificially prepar products are known as "phosphors," and the fluorescence is frequently associated with the presence of a foreign ingredient at a very low concen tration - a fraction of 1 percent. The light emitted during rediation by t exciting source is known as "fluorescence." Often, the fluorescent sub stance continues to emit light for a time after the exciting source is ext guished. Such a decaying emission of light is known as "phosphorescen

A ground and polished filter of dark ultraviolet transmitting glass front of a quartz arc holds back the visible light emitted by a mercury-

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4/ Reproduced from the Denver Equipment Co.'s monthly organ for Ap 1940 and prepared for it by the Hygrade Sylvania Corporation, Sal Mass.

5/ Fonda, G. R., Elec. Eng., vol. 58 December 1938, pp. 677-681.

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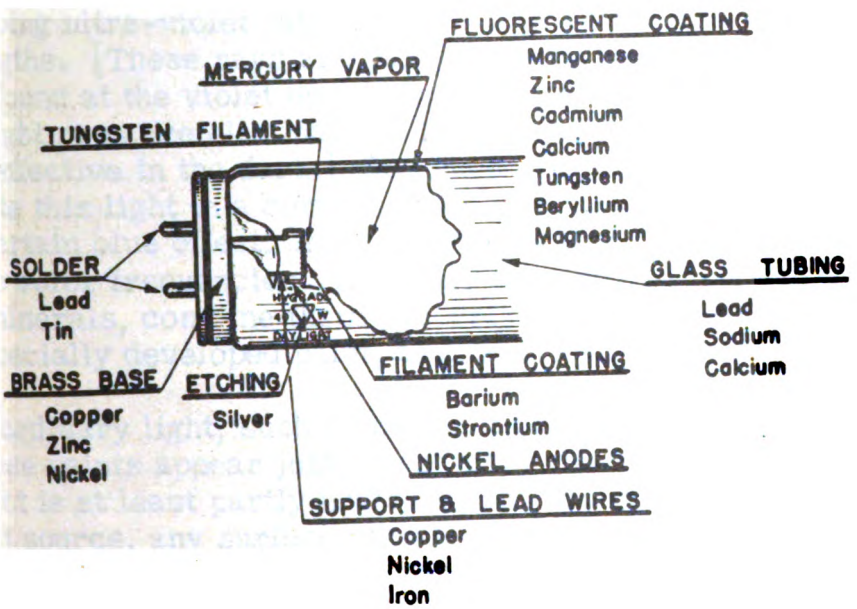

Figure 1.--Minerals in the fluorescent tube of the Hygrade Sylvania Corporation, Salem, Mass. (From Denver Equipment Co.'s Deco Trefoil, April 1940.)

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burner and allows only a concentrated beam of invisible ultraviolet radiations to pass, thereby producing what has been termed a "black ray." Various common substances obsorb these invisible radiations, change (increase) their wave lengths (these all travel at the same speed in free space), and re-emit them as colored light visible to the eye. This light emission is fluorescence.

Hartman 6/, Philadelphia maker of luminous paints, explains fluorescent lighting as follows:

> Certain mineral substances possess the rare property of absorbing ultra-violet rays and re-emitting them in longer wave lengths. [These rays are part of the invisible spectrum and are found at the violet end, being observable only when all visible light rays are eliminated. Therefore, this luminescence is most effective in the dark.] One such mineral substance will re-radiate this light in a certain shade of red, another will produce a certain blue effect, and so on throughout the entire band of visible color frequencies. It is only necessary to select the proper minerals, combine them properly, and use them as pigment in this specially developed paint, to create any desired color effect.
>
> In ordinary light, such as daylight or incandescent electric light, these paints appear just as ordinary pale tints. But when other light is at least partly excluded, and violet rays are employed as a light source, any surfaces treated with these colors immediately become fluorescent, and are brilliantly radiated in the form of colored light. However, there is no radio-activity involved, and the paints, the process of illumination, and the whole scheme are entirely harmless to human tissue.

The term "fluorescent lighting" can be used in two respects, according to Costello 7/- first, to describe the new fluorescent tubes, and, second, for "black light" in conjunction with fluorescent paints. When any material is treated with such paints, the white light turned off and the "black light" turned on, the latter will radiate invisible ultraviolet rays, which will cause the fluorescent-treated materials to re-emit light according to the colors of the pigments used in the paints.

6/ Hartman, Frank: Broadcast News, April 1935.
7/ Costello, Charles, Black-Ray Lighting Co., Cleveland, Ohio.

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DEFINITIONS

Some confusion in terminology exists among the various authorities frequently consulted; therefore, in the following an attempt is made to state definitions of luminescence, fluorescence, and phosphorescence that describe the phenomena as they seem to be understood by the fluorescent-lighting industry. Other definitions to be considered are found in (1) Webster's New International Dictionary (Merriam & Co., Springfiel Mass., 1939); (2) Ford's Dana's Textbook of Mineralogy (John Wiley & So New York City, 4th ed., 1932); and (3) Weld's Glossary of Physics (McGra Hill Book Co., New York, 1937). Bryson 8/ considers the distinction between the three terms arbitrary, and his suggestions have been considere in the following definitions.

Luminescence. - This is a broad term covering any emission of light not ascribable directly to incandescence and therefore occurring at low temperatures, as in the firefly. This term includes a long series of phenomena, such as fluorescence, phosphorescence, triboluminescence, chemiluminescence, crystalloluminescence, electroluminescence, cathod luminescence, and thermoluminescence.

Fluorescence. - The property of emitting radiation from within a substance exposed to direct radiation or electrical discharges in a gas-filled or vacuum tube is known as fluorescence. This phenomenon is wel exhibited by the mineral fluorite. The emitted radiation is longer in wav length than the absorbed radiation, and therefore commercial practice applies violet or untraviolet light, X-rays or various electronic bombard ments as the exciting radiation to get emitted radiation in the visible spectrum. After the exciting radiation is discontinued, the fluorescence extinguished at various rates.

Phosphorescence. - When the afterglow of a fluorescent substance exceeds 10^{-8} seconds (and in some instances it lasts for several days), phenomenon is described as phosphorescence - namely, fluorescence th continues for a time after excitation is discontinued.

Phosphors. - Fluorescing and phosphorescing substances are calle phosphors. Most of the industrial applications are with synthesized min or organic substances, because naturally occurring materials have prov too erratic and unreliable.

8/ Bryson, H. Courtney, Luminescent Pigments and Paints: Oil and Co Trades Jour., London, vol. 96, December 1939, pp. 1181-1396 (int mittent); vol. 97, January 1940, pp. 33-139 (intermittent); Februar 1940, pp. 245-247.

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FLUORESCENT LIGHTING

The phenomenon of fluorescence has been familiar to scientists for several hundred years, and the idea of a fluorescent lamp is not in itself a new one. The colored, fluorescent, advertising-sign tubing has been a familiar sight for some years, but until now fluorescence has not been used for general lighting.

The fundamental principle of the fluorescent lamp involves merely transforming electrical energy into invisible ultraviolet radiation and this into visible light by exposing chemical powders, known as phosphors, to the direct rays of ultraviolet or X rays.

The ability of a gas or vapor to become "luminescent," that is, to give off light under the influence of the flow of electrons through it, involves a somewhat intricate theory of the structure of atoms.. Popular explanations of this theory usually resort to the idea of a "collision" of the speedy electrons with the atoms of the gas. When these encounters take place, there is a state of excitation that produces light. To attempt to explain the theory of fluorescence would introduce more complications than are involved in explaining the production of light directly by the flow of electrons through a gas. Materials that do fluoresce have the property of absorbing energy at one wave length and reradiating it at a longer wave length somewhat as do transformers or some radio tubes, which absorb energy at one voltage and current and deliver it at another.

How It Operates

Fluorescent lamps are commonly tubular with an electrode sealed in each end, and are coated inside with special fluorescent powders, which glow when stimulated by short-wave untraviolet light. The dimensions of the tube usually are within the limits 18 to 60 inches in length and 1 to 2-1/8 inches in diameter, but other sizes may become available. The peculiar ultraviolet light (and some visible light) is produced within the tube by a low-pressure electric discharge in mercury vapor (with a little argon present) between two preheated small coils of tungsten wire, which act as electrodes. The resulting fluorescence produces a rich, bright glow, either artificial daylight or a deep, beautiful color, from the entire coated surface of the glass tube.

According to Cox 9/, a method of coating the inside of the lamp deposits the phosphors in a sort of porous film on the walls of the bulb, so that it may

9/ Cox, J. L., Luminescent Coating for Electric Lamps: U. S. Patent 2,096,693, Oct. 19, 1937.

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absorb a relatively greater amount of the ultraviolet energy and deliver a proportionally greater amount of visible light.

Various powders emit their radiant energy at different wave lengths, with the result that a variety of colors can be produced through different mixtures of the phosphor compounds.

In describing his luminous tube, Beck 10/ covers the progress of illumination as follows (his composite "daylight" light is formed by blending neon light, mercury light, and incandescent light):

> The progress of the illumination art and corresponding industry has been marked by well-defined epochs and corresponding inventions. The oil lamp, used as long ago as the dawn of the Christian era, continued to be used until the discovery of illuminating gas. This was superseded by the Edison carbon-filament incandescent lamp. This was followed by the now widely used tungsten-filament lamp, in which a filament of tungsten was substituted for the Edison carbon filament. Toward the end of the nineteenth century and in the early years of the present century, attempts were made to utilize the light emitted when a discharge of electricity is passed through a column of gas at low pressure, for example, air, nitrogen, carbon dioxide, contained in elongated tubes known as Moore tubes. These were commercially unsuccessful, largely because the gas filling became depleted very rapidly. Somewhat more successful were the Cooper-Hewitt mercury-vapor lamps, in which a discharge of electricity occurs between electrodes in an atmosphere of mercury vapor. For special purposes these lamps find application, but they are substantially monochromatic, or at least the spectrum of the light emitted is so predominantly in the blue region that the human skin assumes a ghastly appearance. These lamps are quite useless for general illuminating purposes.
>
> When the rare gases of the atmosphere, for example, neon, became available in commercial quantities, the practically dead art of illumination by discharge of electricity between electrodes in an atmosphere of gas was in a sense born again, because means were discovered whereby a tube having a filling of neon and provided with suitable electrodes would have a period of useful commercial life. But, like the Cooper-Hewitt mercury-vapor lamp,

10/ Beck, Leo L., Luminous Tube: U. S. Patent 2,012,236, August 20, 19

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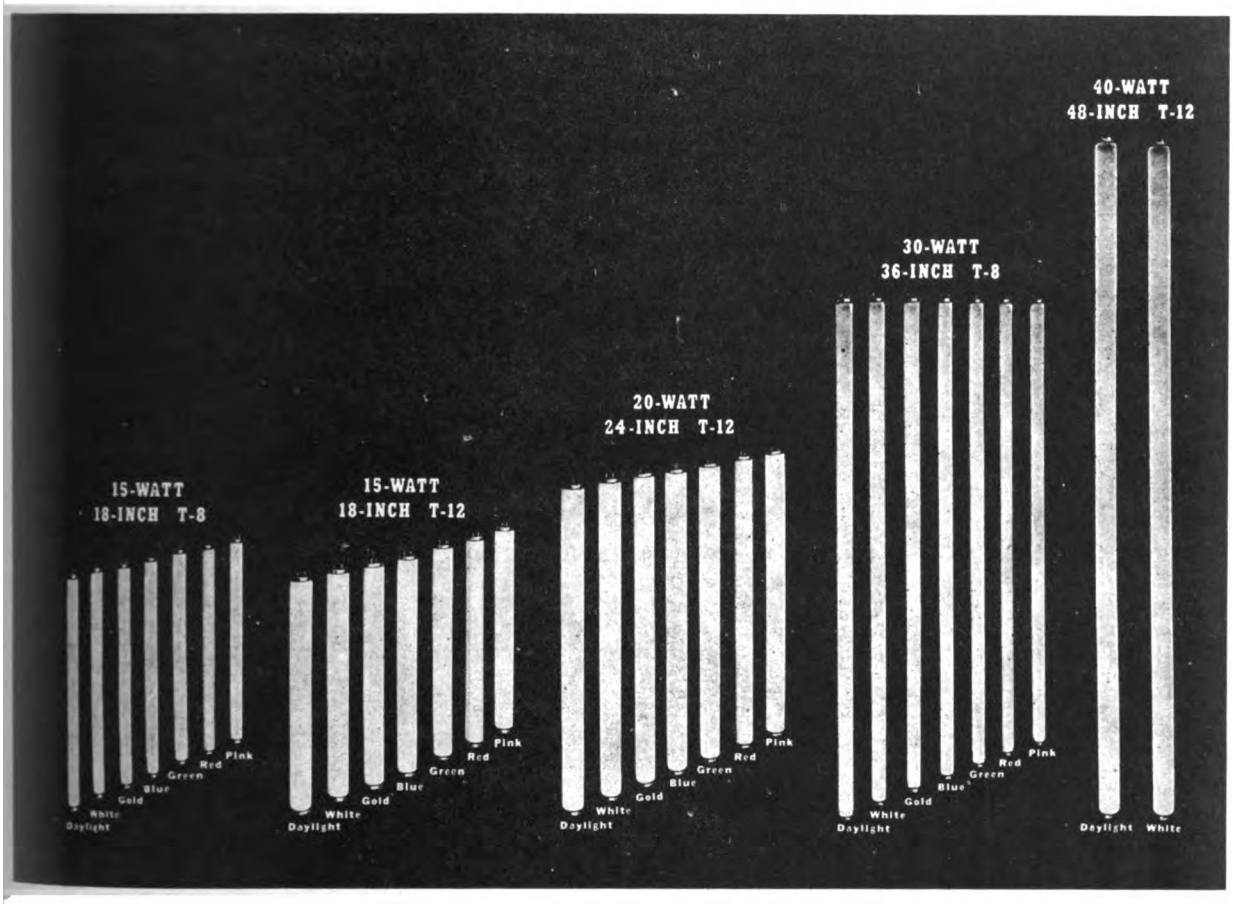

Figure 2.--Fluorescent lamps known as "the fluorescent family" (G. E.). A 9-inch and a 58-inch lamp are to be added. The 18-, 24-, and 48-inch T-12 lamps are 1½ inches in diameter, and the 18- and 36-inch T-8 lamps are 1 inch in diameter. Westinghouse makes five similar sizes. The white lamps are more suitable for illuminating plant interiors, and they are usually placed horizontally.

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the neon tube or lamp emits a substantially monochromatic light in the red end of the spectrum, and while such a light is of great value for display purposes, it is useless as a general illuminant.

Throughout the history of the lamp art, the problem of securing a commercially satisfactory lamp having substanially the same effect as daylight has ever been present.

With the development of the present-day fluorescent tube, this has been accomplished; today, any desired combination of colors may be obtained by careful selection of the minerals to be used for coating the inner walls of the fluorescent tube. In figure 2 11/ is shown a family of fluorescent lighting tubes of the sizes available.

The following advantages for fluorescent lighting have been pointed out:

1. High efficiency. Greater illumination is now possible without increase in consumption of wattage.

2. Cool light. Only one quarter the radiant heat and half the total heat of ordinary incandescent electric lamps of the same light output is emitted. In this way, the load on air conditioning is greatly reduced, and tasks performed under intense light, which formerly were unpleasantly hot for the operator, now can be performed in cool comfort. The operating tubes can be touched without discomfort.

3. Daylight quality. The "daylight" lamp is the most efficient source of artificial daylight available. Indoor illumination without excessive heat, which closely approximates natural daylight, permits color examination and comparison heretofore possible only in daylight or by the use of highly inefficient filters with incandescent lamps.

4. Colored light. Pastel shades of light may be produced directly with the fluorescent lamp.

5. Avoidance of shadows and glare. Instead of an almost point source of light from the incandescent lamp, the fluorescent lamp offers a comparatively glareless tube of light with almost complete absence of shadows.

11/ Courtesy of one of the manufacturers.

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Uses in the Mineral Industry

General Lighting

The fluorescent tube or lamp, whose light is more effective than tha of the incandescent lamp, is used widely in mining plants. The "white" tube, which is somewhat more efficient than the daylight lamp, is preferre for many applications, both because of this and because of its warmer col In contrast with the incandescent lamp, shadows are less intense, the light being well diffused, and when two fluorescent lamps are operated as a pai flicker is almost eliminated.

Fluorescent lamps have a longer life when used more or less continuously and in planning to use them for plant illumination it should be recognized that switching them off and on unnecessarily shortens their lif far more than constant use. The amount of heat emitted by fluorescent tubes is low, and for equal light emission the fluorescent tube consumes approximately one-third the power required by the tungsten incandescent lamp.

It seems probable that the fluorescent lamp will find increased use in mine change-houses, hoisting rooms, power plants, coal-preparation buildings, several types of milling and treatment plants, and in many meta manufacturing operations.

The effects of vibrations are not so serious as with incandescent lamps, but where crushed rock is likely to fly, it would be advisable to pr tect the lamps with wire screening. Good illimination means better and safer work, including less strain on the eyes and easier vision, and it is claimed that fluorescent lighting offers all these.

Regarding the benefits to be derived from better lighting, an editori entitled "Factory Lighting" 12/points out:

> The provision of good lighting is not philanthropy. The right type of lighting in the right place has been shown to result in better-quality work and a higher production rate. And these benefits can often be obtained at a lower cost than if obsolete lighting methods are employed. Some months ago we drew attention to a windowless factory for high-precision engineering work, in which reliance was deliberately placed on artificial light provided by fluorescent tubes.

12/ The Metal Industry, Factory Lighting: London, March 29, 1940.

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Fluorescent lamps are suitable, also, for mine-office and laboratory work - clerical, drafting, and reading of plans. An adjustable "floating" arm or bracket and reflector for an 18- by 1-inch, 15- watt, fluorescent, daylight tube is available for table or desk use. This lamp is cool and does not concentrate the heat, as does the incandescent lamp; in use, the lamp should not be too high above the job.

Extreme variations in temperature lower the efficiency of fluorescent lamps, and therefore, for outdoor illimination, it seems advisable to protect the lamp and to approximate "room temperature."

Mineral Examination

For several years, the value of fluorescence as a means of detecting certain minerals has been recognized. As early as 1916, an ultraviolet apparatus was described by Andrews, 13/ who used a spark-gap as a source of ultraviolet light. For examining tungsten ores, Vanderburg 14/ suggested that ultraviolet rays afford a simple means for determining scheelite ores and mill products. Scheelite fluoresces bright light blue when activated by ultraviolet rays emitted by a high-tension disruptive spark between iron terminals.

Portable equipment for use in mines was described by Vanderburg 15/ as developed jointly by O. F. Heizer 16/ and Paul F. Kerr 17/. The apparatus weighed about 18 pounds, had a small transformer, which stepped up 110 to 120 volts a.c. to 4,500 volts, a mica condenser, and a spark-gap with adjustable and replaceable iron electrodes, as well as switch and other accessories. It was similar to Andrews' design but had a quartz projecting lens and was designed particularly for the detection of scheelite underground. Especially striking in the total darkness of a mine, the fluorescence of this mineral offers a simple and reliable method for qualitative (and rough quantitative) determination. Units of less weight are now commercially available.

In concentrating scheelite ores, such an instrument is useful in estimating the percentages of scheelite in jig, table, and magnetic-separator

13/ Andrews, W. S., Apparatus for Producing Ultraviolet Radiation: General Electric Review, vol, 19, April 1916, pp. 317-319

14/ Vanderburg, W. O., Mining and Milling Tungsten Ores: Bureau of Mines Inf. Circ. 6852, 1935, 47 pp.

15/ Vanderburg, W. O., A Note on the Use of Ultraviolet Lamps in Mines for Rapid Determination of Scheelite in Ores by Fluorescence: Bureau of Mines Inf. Circ. 6873, 1936, 3 pp.

16/ Manager, Nevada-Massachusetts Co., Inc., Mill City, Nev.

17/ Associate professor of Mineralogy, Columbia University, New York.

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products to test their efficiencies. A sample of the dried material is placed under the spark lamp, and the amount of scheelite in the sample c be approximated by its fluorescence. The fluorescence of scheelite does not show as readily in a lighted room on the finer material as on the coarser material. A dark or well-shaded room is necessary for best results. Because chemical methods of assaying for tungsten are slow ar expensive, they are seldom, if ever, used in routine mill-control in tung plants. Ordinarily, methods based upon the specific gravity of the tungs minerals are employed. With scheelite, the ultraviolet apparatus is mor rapid than panning, and, because of the greater area available for exposu it gives a better average.

The New Jersey Zinc Co. also uses this ultraviolet light in the exa nation of zinc-mineral products to control the operation of the concentra machines of their ore from Franklin Furnace, New Jersey.

Instead of the spark gap as a source of ultraviolet light, the argon lamp became available recently as a cheap and simple source. Also, a b fluorescent lamp serves as an effective source. Both of these work dire from the ordinary lighting circuit on 110 volts. However, the amount of light emitted is low (from a 5-watt lamp, it is 1/100 of that of a 125-wat mercury-discharge lamp). To receive adequate excitation, a substance must be placed as close as possible to the lamp.

Another source of ultraviolet light is the mercury-discharge lamp the Cooper-Hewitt type, which is expensive and runs at a high temperatu Until recently, however, it was one of the important sources of ultravio light.

"Black Light"

The recent development of quartz-arc lights with accompanying g filters, identified as "black light," has greatly simplified the problem o obtaining an inexpensive but intense source of ultraviolet light for miner examination as well as other purposes where ultraviolet light alone (with almost no visible rays) is desired. It is available in a simple holder sim lar to that of a "photoflood" lamp, with compact transformer, easily por and constructed so that it can be connected to the regular lighting circui

This improvement eliminates the necessity for constructing a spec box, as described above, and now several commercial units suitable for in mineral examination are available.

The so-called "black light" is attained by placing a filter of dark-colored ultraviolet transmitting glass in front of an ultraviolet quartz-ar

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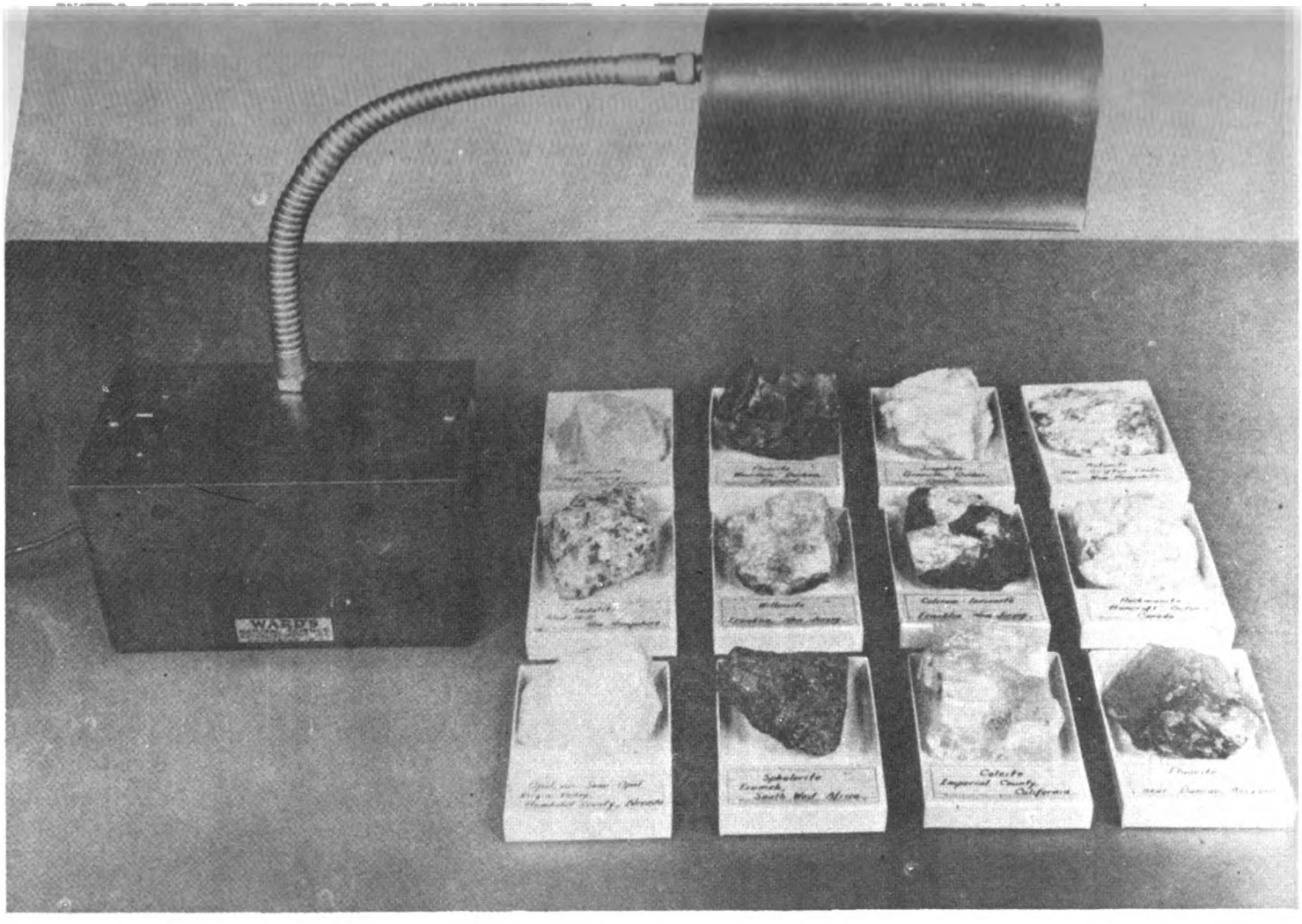

Figure 3.--Black-light lamp for examination of fluorescent minerals.

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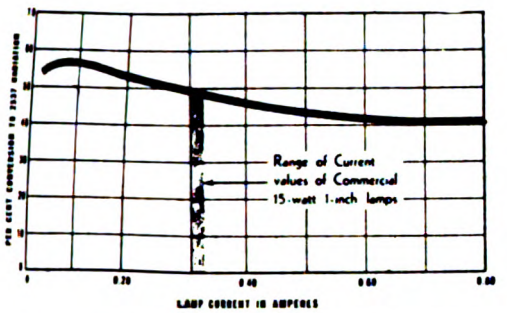

Figure 4.

Conversion to 2537 Radiation

The efficiency of conversion of energy put into a lamp of given diameter to 2537 radiation increases somewhat as the current density is decreased. Although increasing the diameter of the tube while keeping the same current would tend to increase the efficiency, the gain would be offset because of failure to maintain optimum bulb wall temperature. The curve shown here is for a 1-inch tube at 104°F.

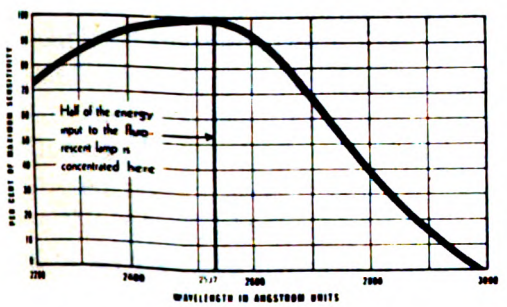

Figure 5.

Sensitivity of Zinc Silicate

For the most efficient operation of fluorescent lamps the phosphor used should have its maximum response at the particular wavelengths of ultraviolet generated. Since no other ultraviolet line of the low pressure discharge in the fluorescent lamp is as much as 4 per cent of the 2537 line, whenever possible phosphors have been selected with their maximum sensitivity between 2500 and 2600A.

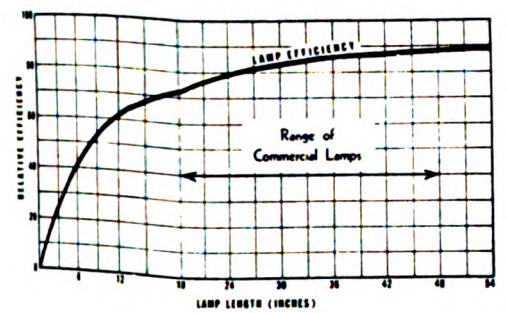

Figure 6.

Effect of Length on Efficiency

The voltage of a fluorescent lamp may be divided into the electrode drop and the potential gradient of the positive column (luminous part of the arc stream). The electrode drop is fixed somewhere between 12 and 18 volts, depending on electrode size, cathode emission, and filling gas. Potential gradient is the voltage required per inch of tube to make up for energy losses and the conversion of energy into radiation. Since the electrode drop remains practically constant, efficiency increases as lamp length is increased, but, as shown, at a decreasing rate.

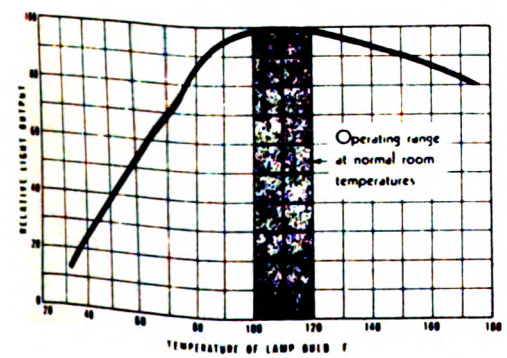

Figure 7.

Effect of Bulb Wall Temperature

At too low temperature the mercury condenses out and the ultraviolet radiation is reduced; at too high temperature the vapor pressure is increased and some of the ultraviolet radiation shifts from 2537A to longer wavelengths. There is also increased reabsorption of the 2537 radiation by the vapor. The adverse effect of low air temperature can be offset to a great extent by protective enclosures. (On page 13 is a graph of the effect of air temperature on the output of bare and enclosed lamps.)

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...ch, which holds back the visible light emitted by the powerful mercury ...arc burner and allows only a concentrated beam of invisible ultraviolet ...diations, ranging between 2,400 A and 4,250 A, to pass.

FLUORESCENT MINERALS

Natural Minerals

Several common minerals, such as calcium, fluorine, and zinc, ...resce when subjected to the influence or excitation of ultraviolet rays. ...her minerals do not themselves fluoresce but do so when certain other ...neral compounds or activators are contained in their composition.

To attain a pure color of specified wave length or combination of ...ve lengths for illumination with fluorescent tubes, minerals of exception- ...ly high purity are required. Natural minerals usually do not have the ...quisite degree of purity. This is evident when it is realized that one part ...foreign matter in ten million is enough to adulterate a mineral and cause ...s rejection as "impure." Rare exceptions of suitable natural minerals ...ay be pointed out, but for practical purposes it is more dependable to ...nthesize the minerals under carefully controlled conditions, so that each ...tch will be as nearly identical to other batches as possible.

Many natural minerals are fluorescent, however, and these will be ...ntioned briefly even though they are not suitable for use by the fluo- ...escent lighting industry.

Calcium minerals. - According to Ford's Dana 18/, several of the ...lcium minerals, especially the calcites, fluoresce. Of these, calcite ...($CaCO_3$) and fluorite (CaF_2) frequently show the property quite strongly; ...to some extent, do aragonite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), scheelite ...($CaWO_4$), and olivine uranite or hydrous phosphate of uranium and calcium ...($Ca(UO_2)_2P_2O_8.8\ H_2O$).

The luminescence of calcite has been known for many years. Some ...stigators found calcite to be active and others found it to be inactive; ...of them held that luminescence is not inherent in calcite but due to ...ces of foreign substance in solid solution. Calcite from Franklin ...rnace, N. J., was subjected to excitation with the iron spark and by ...thode bombardment 19/. The phosphorescence under photo-excitation

18/ Ford's Dana's Textbook of Mineralogy: John Wiley & Sons, New York, ...4th ed., 1932, 851 pp.

19/ Nichols, E. L., Howes, H. L., and Wilber, D. T. The Photoluminescence ...and Cathodoluminescence of Calcite: The Physical Review, vol. 12, ...November 1918, pp. 351-367.

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is of the vanishing type, has a ruddy color, and a duration of about 0.4 second. Under cathode-excitation, the phosphorescence is persistent, red in color, and measurable 300 seconds after excitation. The characteristic ruddy phosphorescence appeared to be due to the presence of traces of manganese. Calcium carbonate artificially prepared is render similarly phosphorescent by the addition of the proper small amount of manganese salt followed by heat treatment.

In describing the preparation of fluorescent calcite, Fonda 20/ ascribed the red fluorescence of the natural calcite occurring at Frankli to the presence of manganese as the activator. The most successful method of preparation was precipitation of the calcium carbonate from solution in the presence of a manganese salt. As the manganese content was increased, the fluorescence rose to a peak and then decreased. Déribére 21/ tested 45 samples of calcareous substances. These also indicate that manganese and strontium are luminogens or activators.

Zinc minerals. - Zinc sulfide or sphalerite, ZnS, and zinc silicate or willemite, Zn_2SiO_4, are the common fluorescent minerals. The form is common, whereas the latter is mined in quantity only in New Jersey associated with zincite, the red oxide of zinc, ZnO, and with franklinite $(Fe,Zn,Mn)O.(Fe,Mg)_2O_3$, a zinc-iron manganese mineral. Willemite is reddish to greenish and under a fluorescent lamp is a brilliant greenish-white.

Other minerals. - Although there are other natural minerals, such as those containing tungsten, barium, strontium, beryllium, and cadmium that show fluorescence, and also the fossil resin, amber (a hydrocarbon mineral), they are not sufficiently important to justify individual consideration.

Synthetic Minerals

It is so difficult to obtain a natural mineral that is relatively pure and contains the correct but small proportion of another mineral, that it has been found simpler and more direct to synthesize the minerals, as mentioned above, and thus obtain the desired combinations and proportio Traces of impurities are very disadvantageous when unwanted and can b avoided by synthesis. Therefore, minerals for use in fluorescent lightin are mostly synthetic, and it is not expected that any substantial tonnage of natural minerals will be mined and consumed directly for this purpos

20/ Fonda, G. R., The Preparation of Fluorescent Calcite: Jour. Phys. Chem., vol. 44, April 1940, pp. 435-439.

21/ Déribére, Maurice, The Luminescent Minerals: Calcareous Substances: Ann. Soc. Geol. Belgique, Bull. 62, 1938-39, pp. 156-

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Bryson 22/ states that commercial phosphorescent pigments are complex phosphors, such as alkaline-earth sulfides, activated by a heavy metal and fluxed with salts. The base material or solvent may be a compound of calcium, barium, strontium, magnesium, beryllium, sodium, or zinc; the activator and the flux, a colorless inorganic salt of low melting point, such as sodium sulfate, potassium sulfate, sodium chloride, borax, or potassium nitrate; a body yielding sulfur, selenium, oxygen, or carbonate; and a reducing agent. Some of these preparations phosphoresce for many hours after illumination.

Zinc sulfide. - Bryson 23/ states that synthetic zinc sulfide is both phosphorescent and fluorescent when properly prepared. It possesses great technical importance and, because it is a simple compound (ZnS), it has received more study than any other luminescent compound. Luminescent zinc sulfide activated with copper is a cream-colored powder fluorescing brilliantly under a "black" lamp and normally exhibiting a fairly long decay period, although not as long as the less-stable phosphorescent strontium sulfide.

In the preparation of zinc sulfide, for example, Bryson states that several processes may be used, but, whatever the method, no metal apparatus should come in contact with the mineral being prepared. A usual procedure involves passing purified hydrogen sulfide into a solution of slightly adidified zinc sulfate, rejecting the first impure precipitate, adding ammonia and sodium to precipitate heavy metals, and then continuing to pass hydrogen sulfide until all the zinc sulfide is down. The copper, generally present to the extent of 0.005 percent, may be coprecipitated or added later. Firing is done in silica or very pure clay boats or crucibles used once and then discarded. Fluxes may be added during the firing.

Beryllium compounds. - For the manufacture of fluorescent tubes, an almost c.p. grade of beryllium oxide is prepared 24/, which is 99.8 percent BeO with impurities not to exceed 0.04 percent CaO, 0.02 percent Al_2O_3, 0.05 percent SiO_2, 0.05 percent Fe_2O_3, and 0.01 percent undecomposed sulfate.

The beryllium oxide is then used in making zinc beryllium silicate and other synthetic beryllium minerals. They are some of the commercially important phosphors.

22/ See footnote 8.
23/ See footnote 8.
24/ Foote Mineral Co., Philadelphia, Pa.

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Important "phosphors." - The number of synthetic minerals used in fluorescent lighting is increasing rapidly, and a complete list is not possible, but the General Electric Co. of Schenectady, N. Y., has tabulated those fluorescent chemicals known as "phosphors" that are most widely used, together with their fluorescent properties:

Fluorescent chemicals (phosphors) 1/

Phosphor	Color	Exciting range A 2/	Sensitivity peak A	Emitted range A	Emitted peak A
Calcium tungstate.....	Blue	2200-3000	2720	3800-7000	4400
Magnesium tungstate..	Blue-white ..	2200-3200	2850	3800-7200	4800
Zinc silicate.....	Green.....	2200-2960	2537	4500-6200	5250
Zinc beryllium silicate	Yellow-white	2200-3000	2537	4500-7200	5950
Cadmium silicate	Yellow-pink	2200-3200	2400	4300-7200	5950
Cadmium borate	Pink	2200-3600	2500	400-7200	6150

1/ In addition to the phosphor, manganese is usually present as an activa
2/ 2200A is the lower limit of measurement.

In modern fluorescent tubes, a mixture of most or all of these phosphors in carefully combined proportions is used, so that the fluorescence produced by the resulting blend will closely approximate the desired "color spectrum."

Activation of Minerals

As previously stated, when certain materials are constituents of some minerals, they become fluorescent. Some impurities are important contributors to luminescence, or they can suppress luminescence. Iron, cobalt, nickel, copper, zinc, manganese, silver, tin, rubidium, antimony, thallium, lead, bismuth, uranium, and samarium are common activators. An activator is an important constituent of phosphors. It should enter the crystal lattice, and widely different amounts are required in the same solvent to obtain optimum results (0.000000024 percent bismuth or 0.04 percent manganese to activate calcium sulfide to maximum brilliance, for example). Iron sometimes is detrimental, 0.00000005 percent being fatal to calcium sulfide phosphors activated with bismuth. One of the most frequently used activators is manganese, and in the minerals used in most fluorescent tubes a trace of manganese salt usually is included.

A recent issue of Collier's 25/shows brilliant color photographs of luminescent materials taken by their own light. Pure willemite and the

25/ White, Owen P., Man-Size Television: Collier's, March 16, 1940, pp. 58-59.

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pure sulfides of barium, calcium, and strontium will not luminesce at all; they require the addition of some other metal, termed an "activator." The amount necessary is extremely small, in some instances as little as 1 part activator in 10 million parts of mineral. It and all other materials used must be as nearly pure as human ingenuity can devise, and all operations are conducted with that in mind.

FLUORESCENT SCREENS

For most purposes, a fluorescent material should have a slow rate of extinguishment, so that its effect will last as long as possible. However, for television screens, a rapid rate of extinguishment is highly important, and the objective is to regulate it so that an image on a particular spot of the screen will last for the fraction of the second until the next cycle and be completely extinguished at that moment, so that no overlap will occur. By glowing for about 1/50 second after excitation, flickerless pictures with more detail become possible 26/.

For viewing the image in the electron microscope, a fluorescent screen (or a photographic plate) is required. When the stream of electrons strikes a fluorescent screen, it produces an image that can be seen by the human eye. Since useful magnifications of 50,000 or even more, in comparison to 2,000 diameters magnification in an ordinary microscope, are obtained, it is important that the fluorescent screen be carefully selected and prepared so that maximum precision may be obtained.

Recently a fluorescent theatre-aisle carpet, in which fluorescent dye was used in preparing the yarn, was installed in a New York moving-picture theatre. It is activated to a visible glow by ultraviolet flash lights carried by the ushers 27/ or by black lamps attached to the seats.

Another novel use for phosphorescent material is for producing echos in a microphone circuit 28/. Here, a fairly rapid rate of extinguishment of the phosphor (complete fading in a few seconds) is desired.

Three classes of fluorescent materials are widely used to convert the electrical energy of the electron beam into light (as, for example, in the cathode-ray tubes used in television receivers) - silicates, sulfides, and tungstates 29/:

26/ Industrial Bulletin of Arthur D. Little, Inc., May 1940.
27/ See footnote 26.
28/ Goldmark, Peter C., Phosphorescent Materials for Producing Echos: U. S. Patent 2,203,352, June 4, 1940. From Science News Letter, July 13, 1940, p. 24.
29/ Monack, A. J., Materials for Vacuum-Tube Manufacture: Ind. and Eng. Chem., vol. 32, No. 8, pp. 1023-1033.

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Silicates. The silicates are stable, relatively high in optical efficiency, and not changed appreciably by small amounts of impurities. The zinc-beryllium silicate system with manganese as an activator, gives a variety of colors from green to deep orange. Zinc silicate (willemite) with a medium persistence green luminescence is used commonly in oscillograph tubes.

Sulphides. The zinc-cadmium sulphide system, activated with silver or copper, gives colors over the entire visible spectrum, from deep blue for zinc sulphide to deep red for cadmium sulphide. Silver activation produces materials with short persistence; copper is used as an activator for materials with long persistence such as oscillograph tubes where it is desired to have a trace remain visible on the screen for several seconds after the electron beam has been cut off. Mixtures of a blue zinc sulphide, activated with silver, and a yellow zinc-cadmium sulphide (or a yellow zinc-beryllium silicate) are used in producing white pictures on television screens. The stability of the sulphides is not so high as that of the silicates, and the former are very susceptible to changes of characteristics resulting from minute traces of heavy metal impurities.

Tungstates. The tungstates are nonactivated fluorescent materials. Their colors vary from a deep blue for calcium tungstate to a light-white for cadmium, zinc, or magnesium tungstates. Their very short persistence makes screens of these materials useful in the photography of high-speed transients."

In London, during the night black-outs, phosphorescent paints are used to reveal the vague general outlines of traffic obstacles and vehicles. Phosphorescent paints 30/ with a period of decay of over 12 hours are desirable to continue to phosphoresce for most of the night after daylight illumination has been withdrawn.

In mines and buildings, the use of phosphorescent paints near the usual electric lamps will provide a faint marker in case power fails and lights are extinguished. A trail of such phosphorescent markers in a mine or a cave should be of value for such eventualities. Phosphorescent knobs on pull-chain switches of electric lights have been known for some time. Important valves, levers, and controllers may be rendered phosphorescent. The safety engineer of a mine or an operating plant, provided with a container of phosphorescent paint, will find numerous places where it's use

30/ Skinner, G. D., Luminous Porcelain Enamel for Signs, Storefronts, and Other Uses: The Enamelist, vol. 17, August 1940, pp. 6-8.

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will increase safety. Phosphorescent employees' badges increase convenience in identification. A board striped with a number of phosphorescent paints which luminesce in different colors, and each color, with a definite period of decay, will constitute a record of time since lights were extinguished or since strong lights passed the recording point. Military uses of phosphorescent paint are numberous. Road signs, traffic hazards, and markers, if phosphorescent, can increase safety.

LUMINESCENT PIGMENTS, PAINTS, AND INKS

Although the manufacture of luminescent pigments and paints consumes minerals, in this paper attention is directed more especially to the use of minerals in the illumination source itself; yet, some reference to it is in order, especially as there are a number of manufacturers of luminous paints and pigments in the United States.

In an extensive technical review of luminescent pigments and paints, Bryson 31/ defines terms and follows with sections on zinc sulfide (see p. 6) and radium paints; the manufacture of alkaline earth phosphors, with its many careful operations, such as proper heat treatment, correct grinding, effect of impurities and activators; effect of temperature; characteristics of some sulfide phosphors (strontium sulfide, calcium sulfide, barium sulfide, zinc sulfide); luminous paints, and how to use them; and concludes with an extensive bibliography of 320 references.

An ever-luminous paint activated by radioactive elements involves the use of fluorescent minerals in combination with the radioactive element to provide a continuous stream of electrons, gammarays, or X-rays to activate the fluorescent minerals, is an old and well-known article. They serve better on objects that usually remain in the dark. Articles and instruments in dark rooms may be marked for convenience in locating them and avoiding accidents as long as the radioactive paint is not to be near stored photosensative film and paper.

Invisible fluorescent ink is used by laundries for indelibly marking shirts and other washables to permit subsequent identification under the ultraviolet light, although the marking is not evident under usual illumination.

The fluorescent screens used in X-ray laboratories for viewing an object directly without waiting for development of the photographic plate are well known. X-rays are of still shorter wave length than ultraviolet light. In taking photographs by X-ray, the radiographs can receive enough effective illumination to justify very short exposure if a fluorescent

31/ See footnote 8.

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intensifying screen is introduced next the photographic film to be caused to glow by the incident energy and increase the amount of effective light. Tasker 32/ recently patented a calcined barium sulfate that can lower the exposure time to 1/50th of the time needed for the bare film alone. The pigment is mounted on paper of suitable size, and the paper is installed behind the photographic film. The barium sulfate must be free of iron, manganese, chromium, copper nickel, or cobalt, but it may contain as much as 10 to 20 percent of the sulfates of strontium or calcium. It is calcined for 6 to 10 hours at 1,000 to 1,060°C. to activate it.

SUMMARY

Minerals play an important part in fluorescent lighting, but their purity must be so great that in almost every instance synthetic minerals must be used. Those that seem to be most useful for fluorescent use are silicate, sulfide, tungstate compounds of zinc, beryllium, and cadmium. A manganese compound usually is present as an activator.

Not only are these minerals used in fluorescent tubes for converting ultraviolet light and X-rays into visible illumination but also to make screens that will convert the energy waves into visible light, and also for the identification of minerals by studying their fluorescent characteristi

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